

## Correlating Moisture Diffusion and Cure behavior of Vinyl Ester Resin / Organoclay Nanocomposites

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Paper Reference Number: 0702-1055

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### Abstract

Vinyl ester resin (VER) is amongst the most widely used thermoset polymers in marine and commercial industries due to its attractive features such as exceptional chemical resistance, thermal stability and mechanical strength. Recently, the application of nanoparticles such as organoclay has led to developing VER based nanocomposites with superior moisture diffusion properties. However, despite the fact that the chemical reactions involve the cure process could largely affect final properties of the cured systems, the investigations concerning the correlation between cure behavior and moisture diffusion of such nanocomposites are rare in open literature. To shed light in this issue, in the present work, rheometry and water diffusivity experiments were conducted on VER/organoclay nanocomposites with various organoclay contents (0-5 wt%). The most interesting point regarding the effect of organoclay on the cure behavior of VER systems was the chemisorption and physisorption of the reacting monomers and initiator molecules on the organoclay platelets surface which is appeared to be responsible for the higher state of cure. Accordingly, comparing the rheological and diffusivity studies indicated that the higher is the cure state, the lower is the equilibrium moisture content. Such phenomenon suggested that the incorporation of the nanoclay could build a perfect network which reduced the water uptake.

**Key words:** Vinyl ester resin, Nanocomposites, Cure behavior, Moisture diffusion.

### 1. Introduction

Today, thermosetting polymers play an important role in industry due to their high flexibility in tailoring desired ultimate properties. Among existing thermoset materials, Vinyl ester resin (VER) have widely used in transportation, infra-structure, construction of parts for automobiles, military ground vehicles and marine applications (Dua et al. (1999), Stone et al. (2000) and Frigione et al. (2004)). The main reasons for such wide acceptability are their low room temperature viscosities coupled with rapid cure schedules and low cost (Dua et al. (1999), Stone et al. (2000) and Frigione et al. (2004)). Recently, the application of nanoparticles such as organoclay has led to the development of novel resin technology which offers the formulators an excellent approach to meeting the needs of today's VER based materials market.

Several research works have been so far published regarding VER / organoclay nanocomposites. For example, Yebassa et al. (2004) investigated the effect of processing parameters on the chemically functionalized clay/VER nanocomposites. They suggested that the addition of styrene as a comonomer and high-intensity ultrasonic mixing produces vinyl ester nanocomposites with the highest degree of clay exfoliation. Furthermore, the viscoelastic properties of VER/clay nanocomposites have been intensively investigated by Drozdov et al. (2003). They found that the response to the uniaxial tensile stress is strongly viscoelastic, whereas increasing the clay content results in a severe decrease of plastic strains observed in pure resin.

However, the addition of organoclay in the VER cure system could result in complex cure process. Therefore, concerning the fact that the chemical reactions involve the cure process largely affect the physical, mechanical and thermal behavior of the cured systems, a good understanding of the parameters which rule the mechanism and rates (kinetics) of VER/organoclay systems cure behavior is the most important prerequisite in process optimization of such nanocomposites (Thomas (2007)). Nevertheless, despite the interest generated in VER / organoclay nanocomposites, to date, the cure kinetics of such systems has been rarely investigated.

The methods mostly employed in the literature to monitor the progress of the cure process are differential scanning calorimeter (DSC) and fourier transform infrared spectroscopy (FTIR). However, DSC method only gives the overall cure kinetics by measuring the rate of produced heat and requires assumptions about the enthalpies of elementary reactions (Lee et al. (2004)). Moreover, FTIR cannot generally detect the increasing consumption of reactive groups at final curing stages (Lee et al. (2004)). Therefore, one could utilize rheological methods to investigate the curing process more successfully in order to overcome these impediments. The techniques not only are crucial for optimization of the processing cycle, but also can be applied to achieve a fundamental understanding the cross-linking between kinetics and the mechanical behavior of the system (Min et al. (1993)).

Therefore, the objective of the present work include evaluation the effect of nanoclay content on the cure kinetics of VER/clay nanocomposite using rheological measurement in isothermal condition.

## **2. Data and Material**

### *2.1. Material*

VER (DERAKANE 470-30) with 33% of styrene monomer was purchased from Dow Chemical Co. (USA). We used Cloisite 30B (C30B) which was a montmorillonite clay organically modified with a quaternary ammonium salt (MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium). Benzoyl Peroxide (BPO), as a thermal initiator was supplied from Fluka and used as received.

### *2.2. Sample preparation*

Vinyl ester resin was mixed with 1, 3 and 5 wt% of C30B using a high shear rotor-stator homogenizer and labeled as VER-1%OC, VER-3%OC and VER-5%OC, respectively. Finally, BPO (1.5 wt%) was added to the mixtures and the compound was stirred for 15 min.

### *2.3. Characterization methods*

SAXS studies were performed on a Hecus S3-Micro focus instrument with an accelerating voltage of 40 KV/30 mA. The data was collected on phosphor image plates at a sample-to-film distance of 40 cm.

Ultra-thin sections were prepared by using a Leica EM FCS cryoultra microtome equipped with a diamond knife. TEM images of VER/clay nanocomposites were obtained at 120 kV, under low-dose conditions, with a Philips 400T electron microscope.

AFM microscopy was performed using a Dualscope/ Rasterscope C26, DME with AC Probe and Aluminum coating Cantilever. All measurements were made at ambient temperature.

Tensile tests were performed to compare the mechanical properties of pure VER and VER/clay nanocomposite samples with the use of a Universal Testing Machine, Model LR 10 K, according to the ASTM D638 at a cross head speed of 100 mm/min and a gripping length of 150 mm. Flexural test were performed on the same machine using the 3-point bending method according to ASTM D790-99. Also, Impact tests on notched specimens were carried out using X CJ-500 Impact Tester (pendulum type) based on ASTM D256. All the results were reported as the average of five experiments for each testing method.

### 3. Results and Analysis

All the cure kinetic studies begin with a basic equation of reactant rate,  $d\theta/dt$ , which is related to the concentration of reactant,  $\theta$ , through a temperature-dependent constant rate of reaction,  $K(T)$ . Although, a variety of models have been proposed so far by different authors (Yousefi et al. (1997), Rogers et al. (2003) and Bullions et al. (2002)), all theories could be generally expressed as:

$$d\theta/dt = K(T)f(\theta) \quad (1)$$

where  $\theta$  is the degree of curing and can be obtained from the time dependent storage modulus ( $G'$ ) using the following equation:

$$\theta = (G'(t) - G'_0) / (G'_\infty - G'_0) \quad (2)$$

where  $G'_\infty$  and  $G'_0$  are the values of the maximum and minimum storage modulus of the crosslinked polymer and also  $G'(t)$  and is the value of the storage modulus at time  $t$ .

There are two primary mechanisms describing the cure kinetics of the most thermoset resins including  $n$ th-order and autocatalytic theories (Yousefi et al. (1997)). The  $n$ th-order model assumes that the reaction rate is proportional to the concentration of unreacted material  $(1-\theta)$ , as shown in Eq. (3), where  $n$  is the order of reaction (Rogers et al. (2003)):

$$d\theta/dt = K(1-\theta)^n \quad (3)$$

On the other hand, in an autocatalytic model, the rate of conversion is proportional to both the concentration of unreacted and reacted material (Rogers et al. (2003)):

$$d\theta/dt = K(1-\theta)^n \theta^m \quad (4)$$

where  $m$  is also the reaction order. In both autocatalytic and  $n$ th-order models,  $K$  represents the temperature-dependent constant rate of reaction obeying the well-known Arrhenius equation (Bullions et al. (2002)) as:

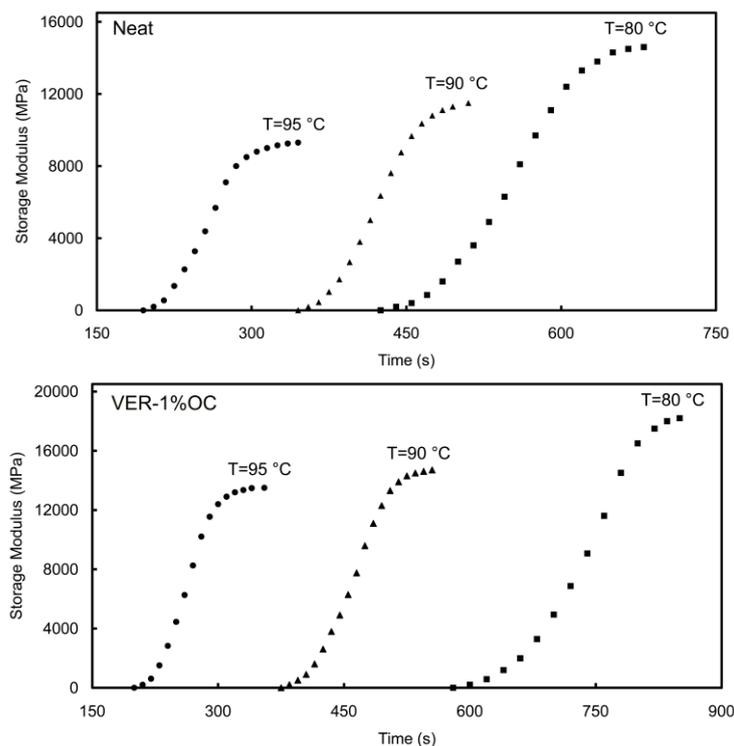
$$K = A \exp\left(\frac{E}{RT}\right) \quad (5)$$

where  $A$  is a frequency factor and  $E$ ,  $R$  and  $T$  are the activation energy, the gas constant and the absolute temperature, respectively.

Commonly, isothermal curing of thermoset material may be the result of more than one type of chemical reaction. In this situation, one reaction may be  $n$ th-order or the other autocatalytic reactions (Bullions et al. (2002)). This combination of reactions can be represented by a generalized expression given by Kamal and Sourour:

$$d\theta/dt = A_1 \exp\left(\frac{E_1}{RT}\right)(1-\theta)^n + A_2 \exp\left(\frac{E_2}{RT}\right)(1-\theta)^n \theta^m \quad (6)$$

Fig. 1 illustrates the isothermal time dependent storage modulus of the VER/clay nanocomposites and that of neat VER at various curing temperatures. The characteristic parameters such as  $G'_{\infty}$ , the onset of curing (the time at which  $G'$  increases) and the whole curing time were determined from the curves as listed in Table 1. It can be clearly understood that for the samples with the same organoclay loadings, the onset of curing and curing time decreases with increasing the temperature. This might be attributed to the availability of more thermal energy for the curing reaction at higher curing temperatures. However, it could be understood that the organoclay nanoparticles are acting as inhibitors regarding to the cure reaction times. It might be because of the fact that the organoclay can capture the reacting monomers and chemically absorb them to their surface. Thereby, the curing reaction is hampered or even inhibited.



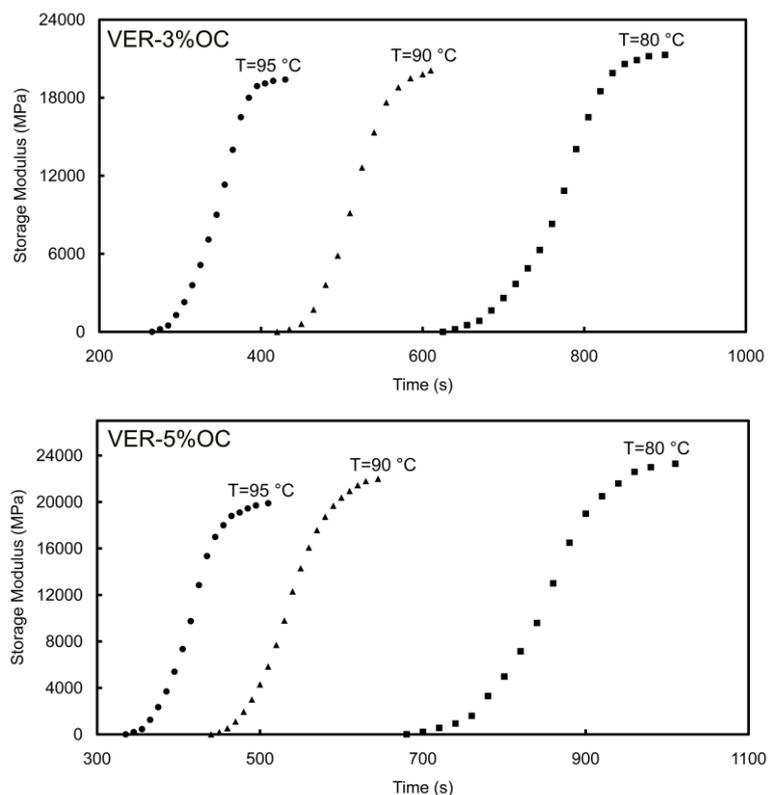


Fig. 1. Storage modulus ( $G'$ ) as a function of cure time for the neat resin and its nanocomposites containing 1, 3 and 5 wt% C30B at analyzed temperatures.

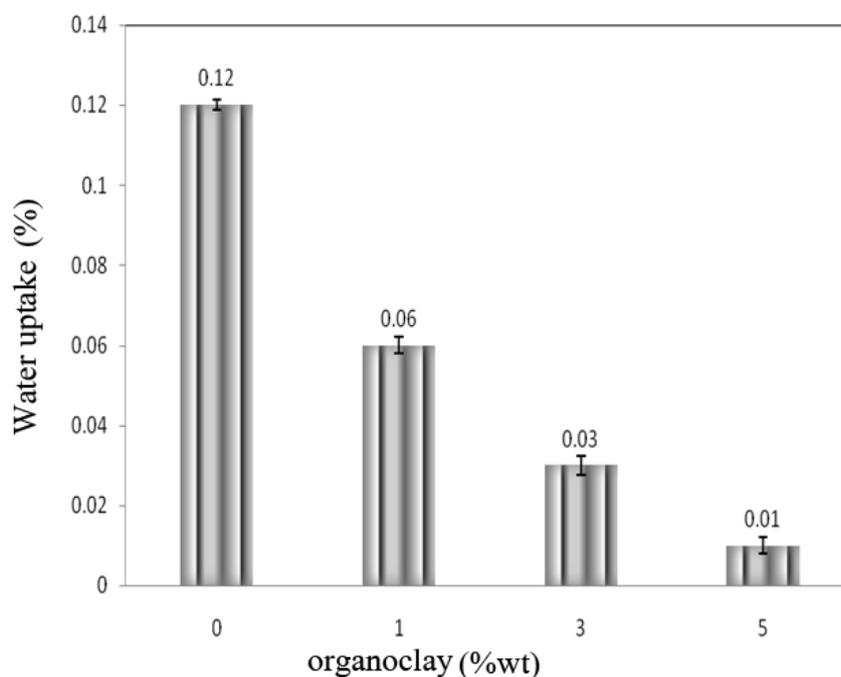
Sample	Curing Temperature (°C)	$G'_{\infty}$ (MPa)	Onset of cure (s)	Curing time (s)	$K_1 \times 10^{-4}$ (s <sup>-1</sup> )	$K_2 \times 10^{-2}$ (s <sup>-1</sup> )	m	n
Neat	80	14600	425	255	8.67	2.71	0.80	0.81
	90	11500	345	165	15.49	3.29	0.76	0.89
	95	9300	195	150	27.41	6.81	0.84	0.95
VER-1%OC	80	18200	580	270	7.77	2.56	0.97	0.78
	90	14700	375	180	13.21	3.27	0.87	0.83
	95	13500	200	155	25.73	4.74	0.72	0.93
VER-3%OC	80	21300	625	275	7.23	2.47	1.40	1.10
	90	20100	420	190	12.02	3.86	0.72	0.95
	95	19400	265	165	20.19	4.37	1.01	0.81
VER-5%OC	80	23300	680	330	5.21	2.20	0.95	1.03
	90	22000	440	205	9.69	3.24	0.83	0.98

	95	19900	335	175	18.45	4.11	1.11	1.15
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**Table 1.** Values of  $G'_{\infty}$ , onset of cure, cure time,  $K_1$ ,  $K_2$ ,  $m$ ,  $n$ ,  $\tau$  and  $\beta$  for the entire samples at the analyzed temperatures.

Furthermore, one can evaluate the kinetic parameters ( $m$ ,  $n$ ,  $K_1$ ,  $K_2$ ) by fitting the experimental data to Eq. (6). The kinetic parameters were determined as listed in Table 2. As expected, the kinetic analysis shows a direct proportionality between both  $n$ th-order and autocatalytic constant rate of reaction and the curing temperature. However, for the systems containing organoclay,  $K_2$  values were higher than  $K_1$  which proves that the autocatalytic mechanism was predominant over the other one. Also, the  $n$ th-order activation energies were found 79, 81, 84 and 87 KJ/mol for neat and 1, 3 and 5% nanocomposites, respectively. Also, the autocatalytic activation energy of the neat resin is 59 KJ/mol whereas the value is 41, 42 and 44 KJ/mol for the VER nanocomposite containing 1, 3 and 5 wt% organoclay.

In addition, as can be seen in Fig. 2, the inclusion of 1, 3 and 5 wt% of organoclay, decreases the water uptake to 50, 75 and 91%. This phenomenon may arise from the penetration of the organoclay into the polymeric chains which, in turn, leads to the occupation of the voids and water diffusion path. Moreover, such occurrence may increase the time needed to reach the equilibrium moisture.



**Fig. 2.** Water uptake percentage of VER nanocomposites as a function of organoclay weight percent.

## 5. Conclusions

This study set out to investigate the cure behavior and mechanical properties of VER based nanocomposites containing various C30B loadings. The influence of the clay

loading and curing temperature on the crosslinking reaction of the prepared nanocomposites was also investigated under isothermal condition. The results showed that the addition of the C30B to VER systems slowed down the curing reaction. However the curing time decreases upon the rising of curing temperature. Also, the modified Kamal-sourour model was found to adequately replicate the kinetic data over the entire cure life. Furthermore, the water uptake of prepared nanocomposites decreased as the organoclay content increased.

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